

Report for 2001RI1801B: Treatment of Roadway Runoff

There are no reported publications resulting from this project.

Report Follows:

1 INTRODUCTION

Many of the current stormwater runoff Best Management Practices (BMPs) are too land intensive to be easily implemented in an urbanized setting. Smaller physical treatment devices, such as oil/sediment separators, that have been widely installed in urbanized areas have been shown not to be efficient enough in removing dissolved contaminants and very fine particulates from the runoff. This is a particular problem with trace metals, most of which are either dissolved or adsorbed to these very fine particulates.

To solve the problem of reducing the trace metal concentration in urbanized stormwater and roadway runoff, researchers in the Department of Civil and Environmental Engineering at the University of Rhode Island have been conducting research on the development of a low-maintenance filtration system designed to be used downstream of an oil/sediment separator. This filtration system will remove not only large particulates but also the dissolved fractions of metals associated with urbanized runoff. The uses of various media for this filter, such as activated carbon and crushed concrete have been explored.

1.1 Objective of Study

The goal of this investigation was to analyze filter media/absorption combinations to optimize the removal of non-settleable trace metals from simulated urban roadway runoff. Using a bench-scale apparatus, influent water spiked with the six trace metals found in Rhode Island roadway runoff that exceeded the EPA National Recommended Water Quality Criteria was pumped through beds of Granular Activated Carbon (GAC)

and Crushed Concrete at a constant loading. Three separate crushed concrete bed depths were first analyzed to determine an optimal bed depth of the concrete media. After this crushed concrete bed depth was determined, one experimental run with both GAC and crushed concrete media took place to determine how much the GAC affected the pH and trace metal concentration of the water before it entered the crushed concrete media. The results found in this study will eventually be incorporated into developing a treatment process to be added downstream of oil/sediment separators that are currently in use in many urbanized areas.

2 BACKGROUND

The Rhode Island roadway runoff characterization report conducted in 1999 confirmed the presence of trace metals in the highway runoff in Rhode Island and provided concentrations for both winter and non-winter conditions. The study found that cadmium, chromium, copper, lead, nickel, and zinc exceeded the National Recommended Water Quality Criteria (Thiem, Bade, and Alkhatib, 1999). These criteria are specified for both freshwater and saltwater bodies, and are reported as the Criterion Maximum Concentration (CMC) and Criterion Continuous Concentration (CCC). The CMC is an estimate of the highest concentration of a contaminant which aquatic life can be exposed to for a short time; the CCC is an estimate of the highest concentration of a contaminant to which aquatic life may be exposed indefinitely (USEPA, 1999). Table 2.1 lists the National Recommended Water Quality criteria of the various contaminants of interest in this study, the range of concentrations found in the Rhode Island roadway runoff characterization report conducted by Thiem et al., and the average concentrations of the trace metals used in this study.

2.1 Metals in Urban and Roadway Stormwater Runoff

Metals found in stormwater runoff make up one of the more permanent contaminants in the environment. In 1998, metals were found to be the second leading pollutant of lakes, reservoirs and ponds in the U.S., and the third leading pollutant of estuaries (USEPA, 2000). Metals are elements, and unlike many pollutants, they cannot be broken down by chemical or biological processes. Since they do not degrade with time, metals may build up in the bottom sediment of water bodies over long periods and gradually enter the food chain.

Trace metals are primarily a concern in stormwater runoff because of their detrimental effects on aquatic life and their potential to contaminate drinking water supplies. Trace metals may be found in natural waters in particulate form by the formation of precipitates, such as hydroxides, sulfides, and carbonates, or by adsorption to clay, silica, or organic particulate matter (Gannon, Bartenhagen and Hargrove, 2001).

A recent study on the constituents in roadway runoff in Rhode Island analyzed the relationships between the constituent concentrations, total suspended solids (TSS), and conductivity. If a constituent had a high degree of correlation with TSS, it indicated that the constituent was present in the particulate form or was adsorbed to particulates in the runoff. If a constituent had a high degree of correlation with conductivity, the constituent was present in dissolved form. The study concluded that cadmium and lead were associated with the particulate fraction in the runoff, nickel was present in dissolved form, and that chromium, copper, and zinc were present in both dissolved and particulate form (Thiem et al., 1998).

2.2 Physical and Chemical Removal Techniques

A large fraction of heavy metals in stormwater runoff adhere to very fine particles of sediment and are subsequently transported with those sediments by the stormwater. Since most contaminants have a strong attraction to suspended solids, the removal of TSS will very often simultaneously eliminate many trace metals from urban stormwater.

In a 1999 study done by Kueddelsmann, a comparison of filtration sand and a GAC/crushed concrete media was analyzed. The filter combination of GAC and concrete removed almost all dissolved trace metals to concentrations below EPA water quality criteria. The filtration sand, however, did not have as high a removal rate for trace metals as did the GAC and crushed concrete combination. It was concluded that the combination of GAC and concrete worked well together because each layer contributed a unique removal mechanism. The dissolved contaminants in the water attaches to the surface of the GAC (adsorption) whereas the concrete causes the soluble contaminants to precipitate due to the change in pH (Kueddelsmann, 1999). However, because of the broad scope of the study, the combination of using GAC and crushed concrete as filtration media was not under much scrutiny. The concrete used by Kueddelsmann was of unknown age and composition, and only approximately 10 empty bed volumes of water were treated by the GAC/Crushed Concrete media. Therefore, additional studies were undertaken to analyze this filtration combination.

In a 2001 study carried out by Robbins, the relative abilities of four combinations of crushed concrete filtration media were compared. The mixtures were hydrated combinations of Portland cement with added high-calcium hydrated lime and/or fine sand

aggregate. It was found that the use of crushed concrete as a filtration medium is a viable method of raising the pH of acidic stormwater runoff over an extended period of time. The addition of hydrated lime, which is commonly used in cement-lime mortars, did not improve the long-term use of the media, and actually appeared to be detrimental. In addition, it was found that there was no significant advantage to omitting the fine aggregate. Therefore it was concluded that the use of an aggregate-containing concrete was effective for treating the runoff (Robbins, 2001).

Based on the results of the past two studies, the promising methods of successfully removing trace metals from urban roadway runoff with adsorption by granular activated carbon and by precipitation using crushed concrete were further analyzed in this study. Aggregate-containing concrete bed depths of 1.5, 3, and 6-inches were analyzed for their removal capacities of trace metals concentrations typically found in Rhode Island roadway runoff. An optimal bed depth was determined based on relationships analyzing the effluent pH, number of bed volumes treated, cumulative mass removed of each particular metal, and metal removal percentages. Once an optimal concrete bed depth was determined, a packed GAC column of the same thickness was placed before the crushed concrete media and both media were analyzed together for their combined removal capacity of the metals.

2.2.1 Carbon Adsorption

In full-scale water treatment by adsorption, activated carbon is used almost exclusively. Activated Carbon is an adsorbent derived from carbonaceous raw materials. Through an “activation process” in which thermal or chemical means have been used to

remove most of the volatile non-carbon constituents and a portion of the original carbon content from the material, a structure results with a high surface area ideal for adsorbing a wide range of compounds. The resulting carbon particles have thousands of small pores, which make it an ideal adsorption material.

Granular activated carbon (GAC) has shown the potential for adsorption of trace metals that are present in dissolved and particulate form in water. For the metals of interest in this study, chromium has been shown to have high adsorption potential, lead and nickel to have fair adsorption potential, and copper, cadmium, and zinc to have low adsorption potential (Montgomery, 1985).

2.2.2 Chemical Precipitation

Another method of removing the non-settleable trace metals found in urban runoff is by chemical precipitation of the metals to form insoluble species. Filtration then can easily remove the resulting precipitates. The most prevalent means of metal precipitation is the formation of insoluble hydroxides, which can be accomplished by merely increasing the pH of the water to be treated.

To achieve chemical precipitation of metals from the runoff, the contaminated water can be passed through crushed concrete to raise the pH. As previously stated, Robbins' research at the University of Rhode Island showed that the use of crushed concrete as a filtration medium was a practical method of raising the pH of acidic stormwater runoff over an extended period of time (Robbins, 2001).

The concrete media serves as a source of hydroxide ions. These ions are transferred from the media to the treated water, thereby increasing the pH of the treated

water. The source of these hydroxide ions comes from the formation of calcium hydroxide in fully hydrated cement. When Portland cement contacts water, a series of chemical reactions occur. Calcium hydroxide (25%) and calcium silicate (50%) make up the two major constituents present in the resulting fully hydrated cement (Kosmatka and Panarese, 1994).

Few studies have been done regarding the long-term ability of crushed concrete to raise the pH of influent water. One study was carried out by the Minnesota Department of Transportation, where they analyzed the pH of effluent water leaching from stockpiles of salvaged crushed concrete of unknown age during precipitation events. Over the course of the 14 month monitoring period, the effluent pH decreased from slightly greater than 10 to slightly greater than 9, with the median effluent pH for the coarse concrete being 9.8, and 9.3 for the fine concrete. The study also stated that these values were above the national recommended water quality criteria for pH, which are 6.5 to 9 for freshwater, and 6.5 to 8.5 for saltwater (USEPA, 1999). The study found that the resulting increased pH would not be a problem because naturally acidic untreated rainwater and runoff would tend to neutralize the alkalinity of the stockpile effluent (Sadecki, et.al., 1996).

Two recent studies were done at the University of Rhode Island analyzing the use of concrete to raise the pH of influent water. In Kueddelmann's study (1999), the highest effluent pH observed from the concrete was slightly less than 11.5. In Robbins' study (2001), the *lowest* effluent pH observed was slightly above 11, with the highest effluent pH of about 12.3. The lower pH in Kueddelmann's study may perhaps have been due to the fact that freshly made concrete was not used in her study, resulting with calcium

hydroxide reacting with atmospheric carbon dioxide. This may also explain the lower effluent pH values seen from the stockpiles of salvaged crushed concrete of unknown age in the Minnesota DOT study. In addition, the crushed concrete was backwashed for several hours prior to each of her experimental runs, thus flushing out the hydroxide ions that may have also caused an initially lower effluent pH. The particle size of the concrete may too have been an issue. Kueddelsmann used a uniform U.S. Standard #4 sieve size for her crushed concrete whereas Robbins used a 16x40 sieve size. The smaller concrete particle size had a larger surface area and may in turn raise the effluent pH higher than the larger concrete particle size.

Kueddelsmann's research also showed a correlation between increasing pH (within the range of pH 7 to 11.5) and percent removal of several trace metals, including cadmium, copper, lead and zinc. The exception to this trend was chromium, for which the removal rate declined at pH values exceeding 10.5 (Kueddelsmann, 1999). The study agreed with values stated in literature that the solubility of many heavy metals is lowest within the range of pH 7-11.5. The solubility of nickel, copper (II), lead (II), and zinc (II) hydroxide is lowest in the range of pH 9-11 with cadmium hydroxide typically lowest for pH values ranging from about 10.5 to 12.5 (Manahan, 2000).

4.2.1 Discussion

The purpose of this part of the experiment was to determine if the GAC would have an effect on the metal removal of the influent water before it is to pass through the crushed concrete column. It was first found that virgin GAC does affect the pH of the water. The water after passing through the GAC had an initial pH of about 10.8, however the pH quickly dropped in the first hour of the run to 8.5 and towards the end of the run

the GAC effluent pH was approximately equal to the influent pH (approximately 5.0). This is likely the reason why there was significant removal of the metals in the GAC earlier in the filter run and not later on when the effluent pH of the GAC was lower. Cadmium, lead and nickel show the highest removal in the GAC at the beginning of the filtration run (when the pH was highest). Copper and zinc show the highest removal in the GAC in the pH range of 8.5-9.0. The pH that exhibited highest removal of the individual trace metals also corresponds to the lowest solubility of the metals. Chromium (VI) shows the highest removal in the GAC around a pH of 6.0. For all metals analyzed, the only significant trace metal removal in the GAC was with chromium, where around 70% removal was typically achieved. The crushed concrete column achieved removal of all other metals. With the combination of GAC and crushed concrete, all six metals analyzed received significant removal in the dual media filter, which is summarized in Table 4.3. Table 4.3 also lists the EPA's Freshwater and Saltwater Criterion Maximum Concentrations of the National Recommended Water Quality Criteria, which were also shown in Table 2.1. The Freshwater and Saltwater CMC's are shown here for comparison with the average final concentrations achieved through the filtration of the dual media. Although the average final concentrations are considerably less than the average initial concentrations, all with the exception of nickel are still not below the Criterion Maximum Concentrations. However, it needs to be emphasized that the concentrations used in this study were based on the extreme trace metal concentrations that were found in roadway runoff.

Contaminants	Average Initial Concentration (µg/L)	Average Total Removal in Dual Filter	Average Final Concentration (µg/L)	Freshwater CMC (µg/L)	Saltwater CMC (µg/L)
Cadmium	18.6	70%	5.58	1	40
Chromium (VI)	67.4	68%	21.6	16	--
Copper	212	45%	117	13	4.8
Lead	66.3	75%	16.6	65	210
Nickel	90.1	67%	29.7	470	74
Zinc	1067	53%	501	120	90

Table 4.3 Summary of Metal Removal in Dual Column

Table 4.4 shows a comparison of the range of pH values that depict the lowest solubility values of the metals of interest along with the pH ranges that had the highest metal removal in this study. Generally, the pH range that had the highest metal removal also corresponded to the pH range that had the lowest solubility of that metal.

Contaminants	Lowest Solubility Range (Metcalf & Eddy, 2002)¹	pH Range of Highest Removal
Cadmium	10.5-12.5	10.5-11.5
Chromium (VI)	<7.0	5.0-6.5
Copper	8.0-10.5	8.0-11.5
Lead	8.5-10.5	10.5-11.5
Nickel	8.5-11	10.5-11.5
Zinc	8.5-10.5	8.5-11.5

¹ Chromium (VI) Solubility from Moore and Ramamoorthy, 1984)

Table 4.4 Comparison of Solubility with pH Range of Highest Metal Removal

The dual-media filter achieved an average overall metal removal in the range of 45-75% depending on the particular metal. It was confirmed that the pH range of highest metal removal also corresponded with the lowest solubility range of that particular metal. Although the average final concentrations were still not below the Criterion Maximum Concentrations for fresh and saltwater, they were still considerably less than the average initial concentrations. However, the concentrations used in this study were based on the

extreme trace metal concentrations that were found in roadway runoff, not the typical or average concentrations. It should also be noted that the loading rate used in this study was higher than what would typically be used. A lower loading rate would result in an increased metal removal. Overall, based on the results obtained in this study, it is concluded that the bed depths used here would better remove trace metals in urban roadway runoff than the BMPs currently in practice.

5 CONCLUSIONS AND RECOMMENDATIONS

Three varying bed depths of a crushed concrete media and a combination of GAC and crushed concrete media were analyzed for their removal capacity of various trace metals in simulated runoff using a bench-scale apparatus. It was concluded that 3 inches of crushed concrete is sufficient to achieve trace metal removal over an extended period of time. Deeper bed depths show no increased benefit of metal percentage removal in the same effluent pH range. However, too shallow a bed depth was found to lead to quicker bed exhaustion and lesser metal removal percentages. Of the six trace metals analyzed, all except chromium achieved significant removal in the crushed concrete columns.

In the dual media column, it was found that fresh GAC does initially cause removal of many of the metals of interest. However, this does not occur for a long period of time and would not occur at all if the GAC was washed prior to filtration. Additionally, the GAC showed an adsorption affinity towards chromium, which was not significantly removed by the individual crushed concrete columns. Therefore, the combination of GAC and crushed concrete is a viable option for the removal of trace metals in urban roadway runoff.

Further research should be done on controlled concrete mixtures of known composition and age to determine their acid neutralization capacities over long periods of time. Additionally, the recovery aspects of crushed concrete should be analyzed in more detail. It would be interesting to see if a relationship exists between recovery of the acid neutralization capacities of the crushed concrete media with the amount of rest time between storm events.

The micro column study should be continued on the dual media to analyze organic removal by the filter. In addition, research should be done on various types of GAC and at various bed depths to optimize removal of contaminants in urban roadway runoff. Finally, a pilot study should be implemented in an urbanized setting to investigate the filter's contaminant removal capacities of actual runoff.

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